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METHOD FOR FORMING COATING EXCELLENT IN EDGE COATABILITY
[Edji hifukusei ni sugureta tomaku keisei hoho]

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Title of Invention: Method for Forming Coating Excellent in Edge Coatability

Claim(s)

(1) A method for forming a coating excellent in edge coatability characterized by coating a water-based coating material containing a thermosetting resin and colloid-like silica on a metal raw material.

(2) The method for forming a coating excellent in edge forming properties characterized by further coating a thermosetting resin top coating material on the surface of the coating of Claim 1.

Detailed Specifications

Field of Industrial Application

The present invention relates to a novel method for forming a coating, and in particular, a method for forming a coating that is ideal as a method for coating a metal raw material having edge parts, such as a wheel of a disk system made from aluminum alloy cast metals which is a tire attachment member for an automobile (hereinafter abbreviated as "aluminum wheel").

Prior Art and Problems Thereof

Wheels for cars have been primarily made from steel in the past, but in recent years they are being replaced by aluminum alloy cast metals which are outstanding in lightweightedness, corrosion resistance, designability, etc. Organic solvent-type thermosetting

*Numbers in the margin indicate pagination in the foreign text.

acryl resin-based coating materials and the like are normally coated for the reason, among others, of enhancing the aesthetic properties and weatherability.

In addition, upon improving the design and so forth, an aluminum wheel has numerous parts with acute angles, e.g., edge parts. If a conventional acryl resin-based coating material or the like is coated on such a material, the aesthetic properties and the like of the flat portions are improved, but the coating material flows at the edge parts during baking and it is difficult to form a coating. Therefore, rust filaments are generated at the edge parts thereof, which progress into serious defects in that the outstanding aesthetic properties are lost. Although eliminating the parts with acute angles by polishing the edge parts is effective as a solution for these defects, it takes too much time and labor; hence, it is difficult to incorporate polishing into a production line, and moreover, polishing may not be preferable from a design standpoint per se. /2

Moreover, in order to improve the corrosion resistance of the edge parts, an organic solvent-type coating material (see publication of Tokukai JP-A No. S64-4660), in which a fine powdered silica was compounded with a thermosetting resin, has already been offered by the present patent applicant. However, this contains a large amount of organic solvent, which is not preferable from the standpoint of environmental hygiene or fire safety. In addition, using, as a coating material which does not contain an organic solvent, a coating

material obtained by compounding a composition in which a fine powdered silica was compounded with a coating material in which a thermosetting polycarboxylic acid resin was neutralized with a basic compound, which was dispersed in water, has been considered. But if the solvent concentration is high, this coating material has drawbacks because since the fine powdered silica exists as an aggregate therein, the thixotropy is high, the viscosity is high, and the coating workability during spray coating and the like deteriorates. In addition, there are drawbacks with a coating material diluted with water to the extent that it can be coated because the solid content of the coating material decreases appreciably and a coating that is outstanding in edge corrosion resistance is not obtained.

Means for Solving the Problems

As a result of meticulous research, an inventor of the present invention discovered that a coating having excellent coating formability with respect to the edge parts and outstanding in smoothness, adhesiveness, corrosion resistance, physical properties, and the like without a large amount of organic solvent volatilizing into the air during coating and baking, and moreover, without the coating material applied to the edge parts flowing during baking could be formed.

That is, the present invention relates to a method for forming a coating excellent in edge coatability characterized by coating a

water-based coating material containing a thermosetting resin and colloid-like silica on a metal raw material, and a method for forming a coating excellent in edge forming properties characterized by further coating a thermosetting resin top coating material on said coating surface.

The water-based coating material used in the method of the present invention contains a thermosetting resin and colloid-like silica as the essential constituents.

The above-mentioned thermosetting resin is composed of a base resin constituent and a curing agent constituent. The base resin constituent comprises an anionic group or cationic group that is soluble or dispersible in the base resin constituent. The base resin constituent and the curing agent constituent may be a mixture, and moreover, they may be in a composition as individual resins in which the curing agent constituent has been introduced into the base resin constituent.

Anionic resins having active hydroxyl groups (e.g., hydroxyl groups, etc.) and anionic groups (e.g., carboxyl groups, sulfonic acid groups, etc.) and active hydroxyl group (e.g., hydroxyl group, amino group, etc.) or cationic group (e.g., amino group, etc.)-containing cationic resins are cited as examples of the base resin constituent used as the above-mentioned mixture. Known resins are already used for all base resins, and vinyl-based resins, polyester-based resins, urethane-based resins, silicone-based resins,

fluororesins, and the like are cited as examples therefor. Among these resins, hydroxyl group and carboxyl group-containing vinyl-based resins and hydroxyl group and amino group-containing vinyl-based resins from which coatings that are outstanding in weatherability and edge corrosion resistance are formed are favorably used. A copolymer obtained by subjecting a (1) hydroxyl group-containing vinyl-based unsaturated monomer, a (2) carboxyl group-containing vinyl-based unsaturated monomer, and as needed, (4) another radical polymerizable unsaturated monomer to a radical polymerization reaction, a copolymer obtained by subjecting a (1) hydroxyl group-containing vinyl-based unsaturated monomer, a (3) amino group-containing vinyl-based unsaturated monomer, and as needed, (4) another radical polymerizable unsaturated monomer to a radical polymerization reaction can be cited as ideal examples of hydroxyl group-containing and carboxyl group-containing vinyl-based resins.

The compounds below are cited as the monomers (1) to (4).

(1) hydroxyl group-containing vinyl-based unsaturated monomer: adducts of hydroxyalkyl (meth)acrylate, (poly)ethylene glycol mono(meth)acrylate, (poly)propylene glycol mono(meth)acrylate and /3 their monomers and lactones, such as ϵ -caprolactone and γ -valerolactone

(2) carboxyl group-containing vinyl-based unsaturated monomer: (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid or

anhydride, carboxyethyl (meth)acrylate, 5-carboxypentyl (meth)acrylate, etc.

(3) amino group-containing vinyl-based unsaturated monomer: aminoalkyl acryl-based monomer, such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate or N-t-butylaminoethyl (meth)acrylate; nitrogen-containing heterocyclic vinyl monomer, such as N-vinyl pyrrolidone, N-vinyl piperidine, N-acryl morpholine or N-acryl pyrrolidine; etc.

(4) another radical polymerizable unsaturated monomer: an alkyl ester having C_{1-11} of methacrylic acid, such as (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate or lauryl (meth)acrylate; an aromatic vinyl monomer, such as styrene, α -methyl styrene, vinyl toluene or p-chlorostyrene; etc.

Polymerization of the above-mentioned unsaturated monomers can be performed in accordance with a known method per se for manufacturing vinyl-based copolymers, for example, by using a solution polymerization method, emulsion polymerization method, or suspension polymerization method. It is advantageously preferable that the polymerization be performed in accordance with a solution polymerization method, and that it can be performed by continuing the reaction on the above-mentioned two constituents for about 1 to about 20 hours, and preferably, about 4 to about 10 hours normally at a

reaction temperature of about 0 to 180°C, and preferably, about 40 to about 170°C in a suitable inactive solvent.

For the solvent to be used, it is favorable to use one which can dissolve the resultant copolymer and be miscible with water so that gelling does not occur during the copolymerization reaction. A cellosolve-based, carbitol-based, glyme-based, cellosolve acetate-based or alcohol-based solvent, among other solvents, can be used as examples of such a solvent. The solvent can be removed under reduced pressure after the water-based coating material is manufactured.

In addition, an azo-based compound, peroxide-based compound, sulfide, sulfine, diazo compound, nitroso compound, and the like can be used as examples of polymerization catalysts.

It is favorable for the hydroxyl group and carboxyl group-containing vinyl-based resin to have a hydroxyl value of about 30 to 200, an acid number of about 20 to 150, and a number average molecular weight of about 10,000 to 100,000.

In addition, it is favorable for the hydroxyl group- and amino group-containing vinyl-based resin to have a hydroxyl value of about 30 to 200, an amine number of about 20 to 100, and a number average molecular weight of about 10,000 to 100,000.

It is not preferable that the hydroxyl value of the above-mentioned resins be smaller than about 30 because the coverability on the edge parts is inferior, or conversely, that it be larger than about 200 because the water resistance and the like deteriorate. In

addition, it is not preferable that the acid number be less than about 20 or the amine number be less than about 20 because while mixing the colloid-like silica constituent, it aggregates and gels, and it is difficult to obtain a stable water-based coating material, or conversely, that the acid number be larger than about 150 or the amine number be larger than about 100 because the coverability on the edge parts, the water resistance, and the like are inferior. It is not preferable that the number average molecular weight be smaller than about 10,000 because the coverability on the edge parts is inferior, or conversely, that it be larger than about 100,000 because the smoothness of the coating deteriorates.

A blocked polyisocyanate compound obtained by blocking, with a blocking agent, such as propanoyl, butanol, hexanol, cyclohexanol, /4 benzyl alcohol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, phenol, methyl ethyl ketone oxime or ϵ -caprolactam, an amino resin obtained from/by a condensation product or a cocondensation product of melamine, benzoguanamine, triazine-based compound, urea, dicyandiamide, or the like and formaldehyde; an alcohol-denatured amino resin obtained by denaturing this amino resin with an alcohol having C_{1-4} ; or a polyisocyanate compound, such as hexamethylene diisocyanate, isophoron diisocyanate, tolylene diisocyanate, xylilene diisocyanate and trimethylol propane triisophoron diisocyanate can be used for the curing agent

constituent used by mixing it with the aforesaid base resin constituent.

From the standpoint of the curability, edge corrosion resistance, weatherability, and the like, a hydroxyl group and carboxyl group-containing vinyl resin/(alcohol-denatured) melamine resin or blocked polyisocyanate compound, hydroxyl group and amino group-containing vinyl resin/blocked polyisocyanate compound are favorable for combinations of the base resin constituent and the curing agent constituent.

The proportion of the base resin constituent and curing agent constituent compounded is such that about 0.5 to 2.0, and preferably, about 0.6 to 1.5 functional groups in the curing agent constituent are compounded per hydroxyl group in the base resin constituent.

A copolymer obtained by subjecting a self-crosslinking unsaturated monomer, such as N-methylolacrylamide and N-butoxymethylacrylamide, to a copolymerization reaction with the aforesaid carboxyl group-containing vinyl-based unsaturated monomer (2), and as needed, the aforesaid hydroxyl group-containing vinyl-based unsaturated monomer (1) and the aforesaid other radical polymerizable unsaturated monomer (4) can be used for the simple resin composition in which a curing agent is introduced into the base resin constituent. It is favorable that this copolymer contain about 5 to 50% by weight of the constituent composing the self-crosslinking unsaturated monomer. In addition, it is favorable that the copolymer

have an acid number of about 20 to 150 or an amine number of about 20 to 100, and a number average molecular weight of about 10,000 to 100,000.

Moreover, in addition to the hereto aforesaid, a hydroxyl group- and carboxyl group-containing vinyl resin, a hydroxyl group- and amino group-containing vinyl resin, or the like which does not substantially contain free isocyanate groups obtained by reacting a compound in which the aforesaid hydroxyl group- and carboxyl group-containing vinyl resin or aforesaid hydroxyl group- and amino group-containing vinyl resin and the aforesaid polyisocyanate compound are half-blocked with a blocking agent can be ideally used. It is favorable that this resin have an acid number of about 20 to 150 or an amine number of about 20 to 100, a hydroxyl value of about 30 to 200, and a number average molecular weight of about 10,000 to 100,000. It is not preferable that the acid number or amine number of the resin be lower than the above-mentioned range because a stable water-based coating material is not obtained, or conversely, that it be higher than the above-mentioned range because the coatability on the edge parts, the water resistance, and the like are inferior. In addition, it is not preferable that the hydroxyl value be smaller than about 30 because the coatability on the edge parts is inferior, or conversely, that it be larger than about 200 because the water resistance and the like deteriorate. It is not preferable that the number average molecular weight be lower than about 10,000 because

the coatability on the edge parts is inferior, or conversely, that it be larger than about 100,000 because the smoothness of the coating deteriorates.

In addition, it is preferable that the elongation of the simple cured coating formed from the aforesaid thermosetting resins be 10% (20°C) or more, and preferably, 20 to 400%, and the glass transition temperature be -20 to 100°C, and preferably, 0 to 80°C. It is not preferable that the elongation be lower than 10%, and moreover, the glass transition temperature be lower than 100°C because the impact resistance deteriorates and the adhesiveness on the raw material is reduced under an environment in which the temperature and humidity change abruptly. Furthermore, it is not preferable that the glass transition temperature be lower than -20°C because if sand, pebbles, and the like collide therewith, there is a drawback because the /5 coating is easily scratched.

The above-mentioned elongation of the coating (tensile elongation at break) is a value obtained when a 20 mm long sample is measured using an all-purpose tensile tester having a constant temperature bath (Autograph S-D, made by Shimadzu Corp.) at +20°C and a tensile speed of 20 mm/min. The sample used in these measurements is obtained by coating a curable resin on a tin plate (thickness: 0.3 mm) to a film thickness of about 60 µm, baked for 30 minutes at 140°C, and subsequently isolated in a mercury amalgam method.

Moreover, the glass transition temperature of the coating was measured using a dynamic [sic] viscoelastometer (Model Vibron DDV-II-EA, made by Toyo Baldwin Co., Ltd.). The sample was prepared in the same manner as used in the measurement of the aforesaid elongation.

The colloid-like silica contained in the aforesaid thermosetting resin is a so-called colloidal silica. A range of 5 to 50 μ , and preferably, 7 to 20 μ is preferable for the particle diameter. One that is supplied as water-based colloidal silica dispersed in water and an organosilica sol dispersed in an organic solvent can be used as is. It is not preferable that the particle diameter be smaller than 5 μ because the viscosity of the coating material is high and the coating workability declines. On the other hand, it is not preferable that the particle diameter be higher than 50 μ because the coatability on the edge parts and the transparency of the coating deteriorate. In addition, the water-based colloidal silica can be used in the state of an aqueous dispersion on either the acidic side or the basic side. Snowtex O and Snowtex OL (both trade names, made by Nissan Chemical Industries, Ltd.), Cataloid SN (trade name; made by Catalysts & Chemicals Industries Co., Ltd.), and the like are cited as examples of colloidal silicas on the acidic side. In addition, a colloidal silica stabilized by the addition of a tiny amount of alkali metal ions, ammonium ions or an amine, e.g., Snowtex 20, Snowtex 30, Snowtex 40, Snowtex C, Snowtex N, Snowtex S, Snowtex

20L (all trade names, made by Nissan Chemical Industries, Ltd.), Cataloid S20L, Cataloid S20H, Cataloid S30L, Cataloid S30H, Cataloid SI-30, Cataloid SI-40, Cataloid SI-50, Cataloid SI-350, Cataloid SI-45P, Cataloid SI-80P, Cataloid SA (all trade names, made by Catalysts & Chemicals Industries Co., Ltd.), and the like are cited for the colloidal silica on the basic side. Colloidal silica has an electrical charge on the particle surface or the particle shell, so the individual particles do not aggregate but are present as independent particles. Thus, even if the solid content of the coating material is high, the viscosity is low and the coating workability is good. In addition, since the viscosity is high during coating, the coatability on the edge parts is good. The above-mentioned organosilica sol is one in which the water-based colloidal silica is substituted with a hydrophilic organic solvent (e.g., methanol, ethanol, propanol, ethylene glycol, etc.), e.g., Organosilica sol MA-ST and Organosilica Sol IPA-ST (both are trade names, made by Nissan Chemical Industries, Ltd.), etc.

The amount of the above-mentioned colloid-like silica compounded is favorably 5 to 40 weight parts, and preferably, 15 to 30 weight parts per 100 weight parts thermosetting resin. It is not preferable that the amount of the colloid-like silica be less than 5 weight parts because the coatability on the edge parts deteriorates, or conversely, that it be greater than 40 weight parts because the

storage stability, coating workability, and the like of the coating material deteriorate.

The water-based coating material used in the method of the present invention can be obtained by adding a neutralizer of an acidic compound or a basic compound to the resin organic solution obtained by dissolving or dispersing the aforesaid thermosetting resin in a hydrophilic organic solvent. An aqueous resin solution is obtained next by performing dissolution or dispersion of the resultant neutral resin in water, after which the colloid-like silica is added thereto and mixed. In addition, it is also obtained in another method by neutralizing and subsequently dispersing in /6 water a mixture obtained by adding and mixing the colloid-like silica with the above-mentioned neutral resin or the resin organic solution before neutralizing, and adding the colloid-like silica before neutralizing. Acidic compounds, such as acetic acid, hydroxyacetic acid, lactic acid, butyric acid and formic acid; and basic compounds, such as ammonia, monoethylamine, diethylamine, triethylamine, monoethanolamine, diethanolamine, pyridine, piperidine and ammonia, are cited as ideal examples of the above-mentioned neutralizer. Moreover, cellosolve-, carbitol-, glyme-, cellosolve acetate- and alcohol-based solvents, and the like are cited as examples of the above-mentioned hydrophilic organic solvent. Conventionally-known additives, pigments, and the like for coating materials can be compounded, as needed, with the water-based coating material.

The method of the present invention can be carried out by applying the aforesaid water-based coating material. Aluminum, iron, copper, tin, zinc, their alloys, and the like can be used for the metal raw material. It is favorable that from out of these materials, a car wheel be made of an aluminum alloy cast metal and that the coating material be applied to a metal raw material that was short brush treated and subjected to a conversion treatment after machining (chromium-, nonchromium-based, etc.). The solid content of the water-based coating material thus applied favorably ranges from 15 to 50% by weight, and preferably, 15 to 40% by weight. It is not preferable that the solid content be lower than 15% by weight because the coatability on the edge parts is inferior, or conversely, that it be higher than 50% by weight because the coating workability deteriorates. In addition, a spray coating means, such as an air spraying, airless spraying or electrostatic coating, is especially preferable for the coating step. Coating is done so that the coated film thickness in the smooth portions is a dried film thickness of normally 10 to 50 μm .

In the method of the present invention, a finished cured coating can be obtained by performing baking after coating the water-based coating material on the above-mentioned metal raw material. Baking can be performed at about 100 to 180°C, and preferably, 120 to 150°C, for about 10 to 60 minutes, and preferably, about 20 to 40 minutes.

In addition, in the method of the present invention, a multilayered coating can be obtained by performing baking after further coating a thermosetting topcoat coating material on the above-mentioned cured coating or an uncured coating which has not been subjected to the above-mentioned baking.

This thermosetting topcoat coating material is favorably a thermosetting acryl resin-based coating material which forms a cured coating whose elongation falls in a range of 3 to 30%, preferably, 5 to 20%, and more preferably, 5 to 15%, and moreover, whose glass transition point is 60 to 130°C, and preferably, 60 to 110°C. It is neither preferable that the elongation of the coating be less than 3% because the flexibility is unsatisfactory, cracking readily occurs, nor that it be larger than 30% because the coating hardness is not sufficient, while on the other hand, that the glass transition temperature be lower than 60°C because the coating becomes soft, or that it be higher than 130°C because the flexibility decreases. (The elongation and glass transition temperature show the same meanings above.) Specifically, a well-known thermosetting acryl resin-based coating material which forms a coating having the above-mentioned physical properties and is outstanding in finished appearance (sharpness, smoothness, gloss, etc.), weatherability (gloss-maintaining characteristics, color retention, chalking resistance, etc.), chemical resistance, water resistance, humidity resistance, curability, and the like may be used in any given form, such as an

organic solution type, nonaqueous dispersion type, solution (dispersion) type, powder type or high-solid type. For example, a coating material in an above-mentioned form comprised by using, as the curing agent, at least one kind of compound selected from an amino resin, urea resin, polyisocyanate compound, block polyisocyanate compound, and the like as the curing agent in an acrylic resin having at least one functional group selected from a hydroxyl group, glycidyl group, etc. (a number average molecular weight that ranges from about 10,000 to 100,000, a hydroxyl value that ranges from 15 to 100, and an acid number that ranges from 0 to 15 are suitable) is cited therefor.

A method for coating the thermosetting topcoat coating material is performed according to the same method as the one for the /7 aforesaid water-based coating material. The coated film thickness is preferably 20 to 80 μm , and in particular, 25 to 60 μm on the basis of the cured coating.

Moreover, baking differs depending on the-type of coating material, but normally, it is performed at about 120 to 180°C, and preferably, 130 to 150°C for about 10 to 60 minutes, and preferably, about 20 to 40 minutes.

Practical Examples

The manufacturing examples, practical examples and comparative examples related to the present invention are described next,

providing "part(s)" and "%" in the manufacturing examples, practical examples and comparative examples are weight standards.

<Manufacturing Example 1> Manufacture of water-based coating material

1

A reaction vessel was charged with 55 parts isopropyl alcohol, the temperature was maintained at 80°C, a mixture of 12 parts styrene, 27 parts methyl methacrylate, 20 parts n-butyl acrylate, 14 parts 2-hydroxyethyl acrylate, 20 parts N-butoxyethyl acrylamide, 7 parts acrylic acid and 1.0 part azobisdimethyl valeronitrile was next added dropwise to this over the required 3 hours, the system was kept at this temperature for 1 hour after the addition was finished, then 1 part azobisdimethyl valeronitrile and 13 parts butyl cellosolve were added dropwise, and the reaction was continued for 4 hours at 80°C to obtain an acryl-based copolymer solution having a solid content of 60%, a number average molecular weight of about 35,000, an acid number of 54 and a hydroxyl value of 68.

Next, 7 parts triethylamine were added to 167 parts (solid content: 100 parts) of the resultant acryl-based copolymer solution, mixed homogeneously, and deionized water was added to obtain a 30% water-based coating material.

<Manufacturing Example 2> Manufacture of water-based coating material

2

Except for replacing the N-butoxyethyl acrylamide in the acryl-based copolymer solution used in the above-mentioned water-based

coating material 1 with n-butyl methacrylate, manufacture was performed as with the aforesaid acryl-based copolymer solution to obtain an acryl-based copolymer solution having a solid content of 60%, a number average molecular weight of about 30,000, an acid number of 54 and a hydroxyl value of 78.

30 parts (solid content) of Cymel 350 (trade name; made by Mitsui Cybel Ltd.; methylated melamine resin) and 7 parts triethylamine were added to 116 parts (solid content: 70 parts) of the resultant acryl-based copolymer solution and mixed homogeneously, and deionized water was subsequently added to obtain a 30% water-based coating material 2.

<Manufacturing Example 3> Manufacture of water-based coating material
3

27 parts n-butyl alcohol and 27 parts isopropyl alcohol were placed in a reaction vessel and heated to 90°C. Next, a mixture of 25 parts styrene, 35 parts 2-ethylhexyl methacrylate, 25 parts hydroxypropyl methacrylate, 15 parts N,N-dimethylaminoethyl acrylate, and 3.5 parts isobisisobutyronitrile was added dropwise to this solution over approximately 2 hours. The reaction was performed under nitrogen injection. The reaction temperature was maintained at 90°C, and further, a 4-hour reaction was performed to obtain an acryl-based copolymer solution having a number average molecular weight of about 15,000, an acid number of 107, an amine number* of 53, and a solid content of 65%.

Amine number*: About 0.5 g of the above-mentioned resin solution is collected, diluted with ethanol, subsequently titrated with 0.1 NHCl, and the amine number is found according to the next expression.

Amine number=
$$\frac{(0.1 \text{ NHCl consumed amount (mL)}) \times 0.1 \times 56.1}{\text{sample amount (g)} \times [(S (\% \text{ by weight}) / 100)]}$$

f in the expression denotes the titer of 0.1 N HCl and S denotes the resin solid content, respectively.

30 parts Takenate B-870-N (trade name; made by Takeda Pharmaceutical Co., Ltd.; ϵ -caprolactam block isophoron diisocyanate) were next mixed with 108 parts (solid content: 70 parts) of the resultant acryl-based copolymer solution, 1.0 equivalent of acetic acid with respect to the amine number was then added and mixed homogeneously, after which deionized water was added to obtain a 30% water-based coating material 3.

<Manufacturing Example 4> Manufacture of water-based coating material 4

/8

85 parts phthalic acid, 10 parts trimellitic acid, 107 parts neopentyl glycol, 70 parts trimethylol propane and 107 parts coconut oil fatty acid were allowed to react to obtain an alkyd resin having an oil length of 30%, an acid number of 40, and a hydroxyl value of 65.

30 parts of Cymel 350 (same one as mentioned above) and 5.0 parts triethylamine were added to 70 parts of the resultant alkyd

resin and mixed homogeneously, and deionized water was subsequently added to obtain a 30% water-based coating material 4.

<Manufacturing Example 5> Manufacture of organic solvent-type coating material

A reaction vessel was charged with 55 parts xylene, the temperature was maintained at 80°C, a mixture of 12 parts styrene, 33.5 parts methyl methacrylate, 20 parts n-butyl acrylate, 14 parts 2-hydroxyethyl acrylate, 20 parts n-butoxyethyl acrylate, 0.5 parts acrylic acid and 1.0 part azobisdimethyl valeronitrile was next added dropwise to this over the required 3 hours, the system was kept at this temperature for 1 hour after the addition was finished, then 1 part azobisdimethyl valeronitrile and 13 parts butyl cellosolve were added dropwise, and the reaction was continued for 4 hours at 80°C to obtain an acryl-based copolymer solution having a solid content of 60%, a number average molecular weight of about 30,000, an acid number of 3, and a hydroxyl value of 68.

30 parts (solid content) of Yuban 20SE-60 (trade name; made by Mitsui Toatsu Chemicals, Inc.; butylated melamine resin) were compounded with 116 parts (solid content: 70 parts) of the resultant acryl-based copolymer solution next, mixed homogeneously, and subsequently diluted with a xylene/Swazole 1500 (trade name; made by Cosmo Oil Co., Ltd.) mixed solvent (=3/7 (weight ratio)) to obtain a 30% organic solvent-type coating material 5.

<Manufacturing Example 7> Manufacture of organic solvent-type coating material B-1

The viscosity of the aforesaid organic solvent-type coating material 5 was diluted to a viscosity for coating use with a xylene/Swazole 1500 (=7/3 (weight ratio)) mixed solvent.

<Practical Examples 1 to 8>

A raw material wherein a machined wheel made of an aluminum alloy cast metal was treated with Pearlbond BT3753 was spray coated with water-based coating materials A-1 to A-8 to a dried thickness of 25 to 35 μm , this was subsequently baked so that the raw material temperature was maintained at 140°C for 30 minutes, and the resulting coated article was applied to tests for the finished appearance (*4), adhesiveness (*5), impact resistance (*7) and corrosion resistance (*8). In addition, an edge coatability (*6) test was performed on the coating material. The results are shown in Table 2.

<Comparative Examples 1 to 3>

A coated article obtained by spray coating the same raw material, as used in Practical Example 1, with the water-based coating materials A-9 to A-11 in the same way as in Practical Example 1 and subsequently baked was applied to tests for the finished appearance /9 (*4), adhesiveness (*5), impact resistance (*7), and corrosion resistance (*8). In addition, an edge coatability (*6) test was performed on the coating material. The results are shown in Table 2.

Table 2

	主 要 成 分								成 熟 制	
	1	2	3	4	5	6	7	8	1	2
水 泥 用 量	61	62	63	64	65	66	67	68	69	70
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0	0	0	0	0	0	0
灰 砂 比	0	0	0	0	0	0	0	0	0	0
水、灰 砂 比	0	0	0	0	0	0	0	0	0	0
砂 子 含 水 率 (%)	0	0	0	0						

Key:

		Practical Example						Comparative Example	
Water-based coating material									
Finished appearance (*4)									
Adhesiveness (*5)									
Edge Coatability (*6)									
Impact resistance (*7)									
Corrosion Resistance (*8)	General parts							Coating is impossible	
	Edge part								
Elongation of coating (%) (*9)									
Glass transition temperature (°C) of coating (*9)									

The test methods are as follows.

(*4) Finished appearance: This was visually evaluated according to the criteria below.

o: smoothness, gloss and sharpness are excellent.

Ⓐ: smoothness, gloss and sharpness are slightly inferior.

Δ: smoothness, gloss and sharpness are inferior.

*:smoothness, gloss and sharpness are markedly inferior.

(*5) Adhesiveness: One-hundred checkerboard squares 1x1 mm in size were cut with a cutter as far as the aluminum wheel of the material, a piece of pressure-sensitive cellophane tape was stuck to a part thereof and peeled off vigorously, after which the number of

remaining checkerboard squares was examined and evaluated according to the following criteria.

○: 100 pieces remained; ⊕: 90 to 99 pieces remained; △: 50 to 89 pieces; ×: 0 to 49 pieces.

(*6) Edge coatability: In place of the aluminum alloy cast metal wheel material, an L-300 replacement blade for an NT Cutter (trade name of NT Inc.) was used and coated, baked and dried at the same conditions as for the above wheel. This was placed in a saline spray tester for 48 hours, and the presence of the generation of rust on the edge of the blade was observed according to JIS Z-2371, and the following evaluation was made according to the following criteria.

○: No generation of rust recognized at all.

⊕: Slight generation of rust recognized.

△: Generation of rust recognized.

×: Marked generation of rust recognized.

(*7) Impact resistance: As a 500 g weight was dropped from a height of 20 cm at 20°C in accordance with Method 6.13 3B in JIS K-5400 (1976), the damaged state of the film was examined and evaluated according to the following criteria.

○: No fissures or cracks recognized at all.

⊕: Fissures or cracks slightly generated.

△: Fissures or cracks generated.

×: Many fissures or cracks generated.

(*8) Corrosion resistance: According to JIS Z-2371, the step in which the sample was placed in a saline spray tester for 24 hours, after which the coated face was washed with water, and subsequently placed in a constant temperature and constant humidity box (temperature: /10 $40\pm 2^{\circ}\text{C}$, humidity: $85\pm 5\%$) for 240 hours was defined as one cycle. This test was conducted for four cycles. The state of rust filaments generated at the edge parts and the general face outside the edge parts was examined, and evaluated according to the following criteria.

o: No rust filaments recognized at all.

㊦: Slight generation of rust filaments recognized.

Δ: Generation of rust filaments recognized.

x: Marked generation of rust filaments recognized.

(*9) Elongation and glass transition temperature of coating: The water-based coating materials 1 to 4 in which no colloidal-like silica was compounded at all were used as the water-based coating materials. The sample preparation and measurement method were performed on the basis of the aforesaid methods.

<Practical Examples 9 to 16>

The water-based coating materials described in Table 3 were spray coated on a raw material in which a machined aluminum alloy cast metal wheel was subjected to a treatment with Pearlbond BT3753 so that the dried thickness was 25 to 35 μm . This was set aside for 5 minutes at room temperature (20°C), predrying was performed for 10 minutes at 60°C , then this was cooled to room temperature, after

Key:

	Practical Example								Comparative Example	
Undercoat coating material										
Topcoat coating material										
Finished appearance (*4)										
Adhesiveness (*5)										
Edge Coatability (*6)										
Impact resistance (*7)										
Corrosion Resistance (*8)	General parts									
	Edge part									

Advantages of the Invention

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According to the method of the present invention, as described above, advantages are manifested with a coating formed without a large amount of organic solvent being volatilized in that the coatability on the edge parts is excellent and the smoothness, adhesiveness and corrosion resistance are outstanding.